

Removal of Toxic Metals from Water Bodies using *saraca Indica* Leaf Powder : A Novel and Cost Effective Water Treatment Green Technology

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ABSTRACT

Competitive biosorption of tri metallic combination [Cd (II), Cr (III) and Ni (II)] on unmodified *Saraca indica* leaf powder (SILP) was observed and compared with their single metal ion solutions. The adsorption capacities of the metal ions [Cd (II): 0.97 mgg⁻¹, Cr (III): 0.89 mgg⁻¹ and Ni (II): 0.65 mgg⁻¹], when present in combination were tested on SILP. These were found to be lower (10-20%) as compared to single metal ion [Cd (II): 1.19 mgg⁻¹, Cr (III): 1.14 mgg⁻¹ and Ni (II): 0.82 mgg⁻¹] solutions. SILP remove the target metal ions in the selectivity order of [Cd (II)>Cr (III)>Ni (II)]. Regeneration of metal treated biomass was attempted for several cycles with a view to restore the sorbent to its original state. The sorption capacity of the regenerated biomass remained constant after three cycles of sorption process, suggesting that the lifetime cycle was sufficient for continuous application. Kinetic studies revealed that adsorption equilibrium in each case follow first order equation. Experimental findings indicate that SILP has enough potential for the development of a simple, fast and ecofriendly method for decontamination of toxic metals from water bodies.

INTRODUCTION

The vitality of water is mandatory to all forms of life and fundamental for environmental health and management. According to National Water Commission, water is treated as an infinite free good yet aqueous systems are increasingly at risk from pollution, particularly of toxic metals. Fierce competition over water resources has prompted fears that water issues contain the seeds of violent conflict. Toxic metal contamination of aqueous waste streams and ground water poses a major ecological and human health problem, which is still in need of an effective and affordable technological solution. Traditional methods employed for water purification which involve ion exchange, reverse osmosis, solvent extraction etc. prove to be costly and prohibitive for low level waste remediation (Eccles, 1999). The impact of heavy metals on water source is immense and that it is only through promotion of good pollution prevention practices that contamination and deterioration of aqueous system will decrease. The ongoing challenge of providing safe water for drinking purpose to the citizens of the developing world, require urgent action. Thus search for alternate and innovative treatment technique has focused attention on the use of plant materials for heavy metal removal

and has gained important credibility during recent years because of the low cost and excellent performance (Villaescusa *et al.*, 2004). This search has brought biosorption to the foreground of scientific interest as a potential basis for the design of novel wastewater treatment process. Implementation of local environmental tactics to solve local environmental issues is the need of the day.

In continuation of our work on the biosorption of toxic metals in aqueous system using agricultural waste (Kumari *et al.*, 2005, 2006; Sharma *et al.*, 2007a, b) recently, we have explored sorption property of the leaf powder of plant *Saraca indica* (Srivastava *et al.*, 2005, Goyal *et al.*, 2007, 2008) for decontamination of toxic metals from their single metal solutions. The present communication reports the competitive sorption behavior of multi metal cationic species [Cd (II), Cr (III), and Ni (II)] using same biomass as a bioremedial approach for the removal of toxic metals from water bodies.

Saraca indica Linn. (Ashoka), an evergreen tree which can survive heat and desiccating dryness is abundantly available throughout the Asian continent. Various parts of the plant possess multidimensional curative properties (Wealth of India, 2003). However, no studies have been directed so far for its sorption behavior towards toxic metals.

MATERIALS AND METHODS

Biosorbent preparation

Leaves of *Saraca indica* Linn. were collected in May 2004. They were washed repeatedly with water to remove dust and soluble impurities, dried at 65 °C for 24 hours, crushed and finally sieved through (105 µm, 210 µm and 420 µm) mesh copper sieves. *Saraca indica* leaf powder (SILP) was used as biosorbent.

Biosorption studies

Heavy metals of interest in this study were [Cd (II), Cr (III) and Ni (II)]. Sorption studies using standard practices were carried out in batch experiments (triplicates) as functions of particle size (105, 210 and 420 µm), biomass dosage (2.0, 4.0 and 6.0 g), contact time (10, 20, 30 and 40 min), metal concentration (1, 5, 10, 25, 50 and 100 mg/L) and pH (4.5, 5.5, 6.5, 7.5 and 8.5). The contaminated water was prepared using AR grade cadmium nitrate, nickel sulphate and chromium chloride in Erlenmeyer flasks. After pH adjustments, a known quantity of biosorbent was added and finally metal bearing suspensions were kept under magnetic stirring until the equilibrium conditions were reached. After shaking, suspension was allowed to settle down. The residual biomass sorbed with metal ions was filtered using Whatman 42 filter paper. Filtrate were collected and metal concentrations were determined using acetylene air flame Atomic Absorption Spectrometer (Perkin Elmer-3100) using the equation: % Sorption = $(C_0 - C_e) / C_0 \times 100$, where C_0 and C_e are the initial and final concentration of metal ions in the solution.

Biosorption Equilibria

In the present trimetallic combination, sorption of metal is a competitive process between ions present in the solution. In such cases, one of the important physicochemical aspect for the evaluation of the sorption process as a unit operation is the equilibria of biosorption. Therefore, soluble metal fractions of ternary metal ions [Cd (II), Cr (III) and Ni (II)] after SILP biosorption under different experimental conditions were measured to determine sorption capacity. Equilibrium isotherms of target ternary metals were obtained in the concentration range (1 to 100 mg/l) on the optimum biomass dosage (4.0 g) at pH 6.5 and plotted between metal adsorbed (mg) per unit mass (g) of sorbent against concentration. The concentration of metals in the sorbent phase was calculated as: $q = (C_0 - C) V/W$, where C_0 and C denote the initial and equilibrium concentration of metals in the aqueous phase, V is the volume and W is the dry weight of the sorbent (Viera and Volesky, 2003).

In order to define the efficiency of biosorption Lagergren plots were also obtained by conducting kinetic studies (batch) at initial [Cd (II), Cr (III) and Ni (II)] ions concentration. SILP (4.0 g) was suspended in 200 ml of [Cd (II), Ni (II) and Cr (III)] solution of known initial sorbate concentration at the appropriate pH values mentioned above, where maximum sorption was recorded. The mixture was continuously stirred using a magnetic stirrer. Samples were withdrawn at pre-determined time intervals in the range of 10 to 40 min, filtered and analyzed for residual metal ions concentration.

Regeneration studies

It is well known that desorption of sorbed heavy metals and repeated usability of the exhausted biosorbent are of significance from the view point of practical application for the water treatment. With this aim in view, desorption behavior of ternary metals from metal loaded biomass was observed. Studies (batch process) were conducted to desorb the ternary metal ions from loaded biomass by two different (hydrochloric and nitric) acids in the concentration range (0.01 to 0.1 M). Metal loaded biosorbent obtained from our sorption experiments, were transferred to Erlenmeyer flasks and shaken with 50 ml of each mineral acid for 30 mins. The filtrate was analyzed for desorbed metal ions.

STATISTICAL ANALYSIS

Batch experiments were conducted in triplicates (N=3) and data represent the mean value. Correlation coefficient and standard deviations were calculated using SPSS PC+TM statistical package (SPSS, 1983). For the determination of intergroup mean value differences, each parameter was subjected to the student-t test for significance level ($p < 0.05$).

RESULTS AND DISCUSSION

Our earlier experiments performed on the biosorption of Cd (II) and Ni (II) (Srivastava

et al., 2005) and Cr (III) (Goyal *et al.*, 2007) in single metal ion solution using unmodified SILP showed that maximum metal binding occurred at pH 6.5 [Cd (II): 92.60%, Cr (III):85.23 % and Ni (II): 48.20%] (Fig. 1). Further, the comparison of Scanning Electron Micrographs of untreated and metal- treated SILP represented large spherical clusters having a pore area of 6.32 μm^2 in case of native SILP, while dense, agglomerated, etched dendrite type morphology having pore area [Cd (II): 0.72 μm^2 , Cr (III): 0.63 μm^2 and Ni (II): 0.53 μm^2] in metal-treated SILP. Observed aggregation and reduction in pore area of untreated and [Cd (II), Cr (III) and Ni (II)] treated SILP has been ascribed to the liquid phase concentration of metal ions at experimental pH confirming the biosorption phenomenon. We have also reported the records of Fourier Transform Infrared spectroscopic analysis which highlighted amino acid-metal interactions in single metal ion solution, found responsible for sorption phenomenon (Srivastava *et al.*, 2005; Goyal *et al.*, 2007). The aqueous solution of SILP is a heterogeneous complex mixture having various functional groups mainly low molecular weight organic acids (Amino-acids). The proteinaceous amino-acids have a variety of structurally related pH dependent properties of generating negatively and positively charged species and play an important role in the binding of cationic and anionic metal species.

Table 1 presents the soluble ion concentration of ternary metals [Cd (II), Cr (III) and Ni (II)] after biosorption on unmodified SILP using optimum biomass dosage (4.0 g), particle size (105 μm) as function of metal concentration and contact time (30 min) at pH 6.5. Sorption capacity of the biomass, ofcourse, depends on the amount of biomass but not directly proportional. The optimum sorption on the biomass (4.0g) in the present case can be explained on the basis of attainment of equilibrium between adsorbate and adsorbent at the existing conditions rendering adsorbent incapable of further adsorption. In any biosorbent system, there are fixed number of active sites available for sorption. It appears that the presence of larger number of smaller particles for a given biomass weight (4.0g) provide sorption system with an optimum surface area available for metal binding. It is also inferred that smaller the size of particle, greater is the sorption efficiency. The reduction in particle size of the biosorbent from [420 μm to 105 μm] results into the optimum surface area and thereby showing the maximum sorption at biosorbent possessing size of particle (105 μm). Further, maximum sorption occurred at 30 min does not result into the enhancement in the sorption efficiency with further increase in time upto 60 min. It might be due to maximum deposition of metal ions on available sorption sites.

pH condition of the solution is an extremely important parameter in metal biosorption.

It governs a series of phenomenon like site dissociation, solubility, mobility and chemistry of the metals ions. pH affects the selectivity of the biomass to bind a variety of metals. At different pH, binding sites are different. Therefore, it is necessary to identify the functional groups that are actually participating in metal sorption. Keeping above views in mind, pH

Table 1. Soluble ion concentration of ternary metals [Cd (II), Cr (III) and Ni (II)] on unmodified SILP at optimum biomass dosage (4.0 g), particle size (105 µm) as function of contact time and metal concentration at pH 6.5

Initial conc. mg/L (µM)	10 min.	20 min.	30 min.	40 min.
Cd (II)				
01 (01.77) ^a	0.79±0.04 ^{+x}	0.74±0.04 ^{+x}	0.70±0.03 ^{+x}	0.70±0.03 ^{+xx}
05 (08.87)	4.72±0.19 ^{+x}	3.37±0.18 ^{+x}	3.19±0.15 ^{+x}	3.19±0.15 ^{+xx}
10 (17.74)	7.55±0.34 ^{+x}	6.05±0.33 ^{+x}	5.69±0.31 ^{+x}	5.66±0.31 ^{+xx}
25 (44.36)	15.61±0.76 ^{+x}	12.74±0.64 ^{+x}	9.19±0.52 ^{+x}	9.15±0.51 ^{+xx}
50 (88.73)	31.18±1.62 ^{+xx}	25.43±1.37 ^{+xx}	18.70±1.03 ^{+xx}	18.65±1.03 ^{+xxx}
100(177.46)	62.23±3.11 ^{+xx}	50.71±2.43 ^{+xx}	36.31±2.06 ^{+xx}	36.17±2.05 ^{+xxx}
Correlation coefficient (r)	0.96	0.97	0.96	0.98
Cr (III)				
01 (03.84) ^a	01.60±0.09 ^{+x}	01.39±0.07 ^{+x}	01.33±0.07 ^{+x}	01.33±0.07 ^{+xx}
05 (19.23)	07.99±0.37 ^{+x}	06.14±0.34 ^{+x}	05.76±0.29 ^{+x}	05.71±0.29 ^{+xx}
10 (38.46)	12.49±0.66 ^{+x}	11.26±0.58 ^{+x}	10.22±0.52 ^{+x}	10.20±0.51 ^{+xx}
25 (96.15)	31.05±1.38 ^{+x}	26.78±1.13 ^{+x}	24.23±1.07 ^{+x}	24.21±1.03 ^{+xx}
50(192.30)	62.01±2.80 ^{+xx}	52.42±2.36 ^{+xx}	48.39±2.06 ^{+xx}	48.29±2.06 ^{+xxx}
100(384.61)	124.72±5.39 ^{+xx}	104.61±4.80 ^{+xx}	96.55±4.29 ^{+xx}	96.32±4.11 ^{+xxx}
Correlation coefficient (r)	0.97	0.96	0.98	0.99
Ni (II)				
01 ()	01.60±0.11 ^{+x}	01.39±0.09 ^{+x}	01.33±0.09 ^{+x}	01.33±0.09 ^{+xx}
05 ()	13.59±0.39 ^{+x}	11.18±0.37 ^{+x}	7.36±0.31 ^{+x}	04.81±0.31 ^{+xx}
10 (34.12)	33.8±0.68 ^{+x}	27.76±0.59 ^{+x}	17.34±0.54 ^{+x}	17.42±0.54 ^{+xx}
25 (85.32)	57.01±2.92 ^{+x}	53.67±2.45 ^{+x}	50.82±2.26 ^{+x}	50.89±2.06 ^{+xx}
50(170.64)	115.11±3.70 ^{+xx}	106.34±3.56 ^{+xx}	100.12±3.38 ^{+xx}	100.23±3.21 ^{+xxx}
100(341.29)	230.42±6.29 ^{+xx}	202.89±5.45 ^{+xx}	200.7±5.35 ^{+xx}	200.8±5.11 ^{+xxx}
Correlation coefficient (r)	0.94	0.97	0.96	0.98

^a Numbers in parenthesis represent soluble metal concentrations in µM., Standard deviations ±., Mean value difference [initial Cd (II), Cr (III) and Ni (II) loaded versus soluble Cd (II), Cr (III) and Ni (II) (µM)] as a function of Time *significance (p< 0.10), **insignificance (p> 0.10), Metal concentration *significance (p< 0.01), **insignificance (p> 0.01).

profile for metal ion binding was recorded for each metal. The % sorption of trimetallic combination on plant biomass increases as the pH of the solution increased from 3.5 to 7.5. The pH profile for such sorption process shows that metal sorption is a function of pH, exhibiting maximum sorption at pH 6.5. There was no significant difference in sorption behavior with further increase in pH upto 7.5. Investigation on pH variation beyond 7.5 yielded in false increase in sorption which might be due to precipitation carry over of metal ions which starts at pH 7.5.

In each case, data were evaluated at significance value (p<0.05). The maximum percentage sorption calculated for each ion present in ternary mixture [Cd (II): 79.34%,

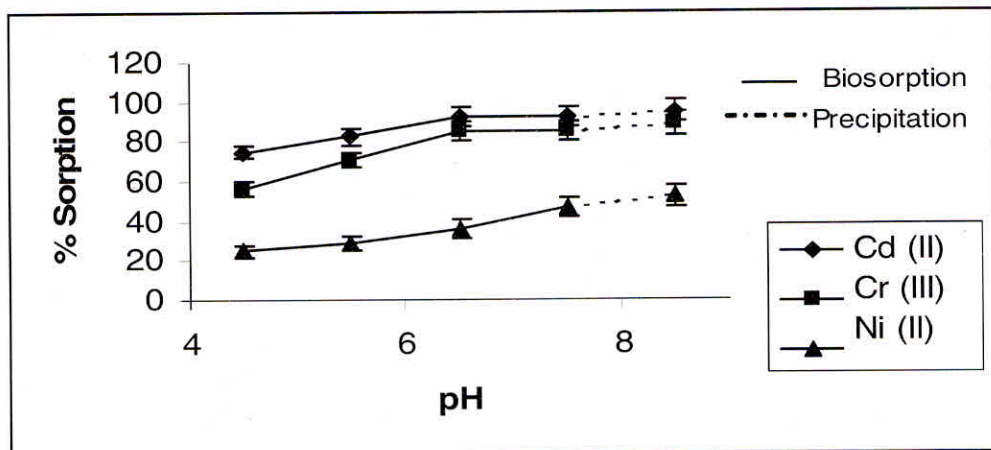


Fig. 1 : Effect of pH on sorption behavior of [Cd(II), Cr(III) and Ni(II)] on SILP in single metal solution. Error bars represent standard deviation of triplicates determination. [C_0 : 25 mg/L; m: 4.0 g; t: 40 min].

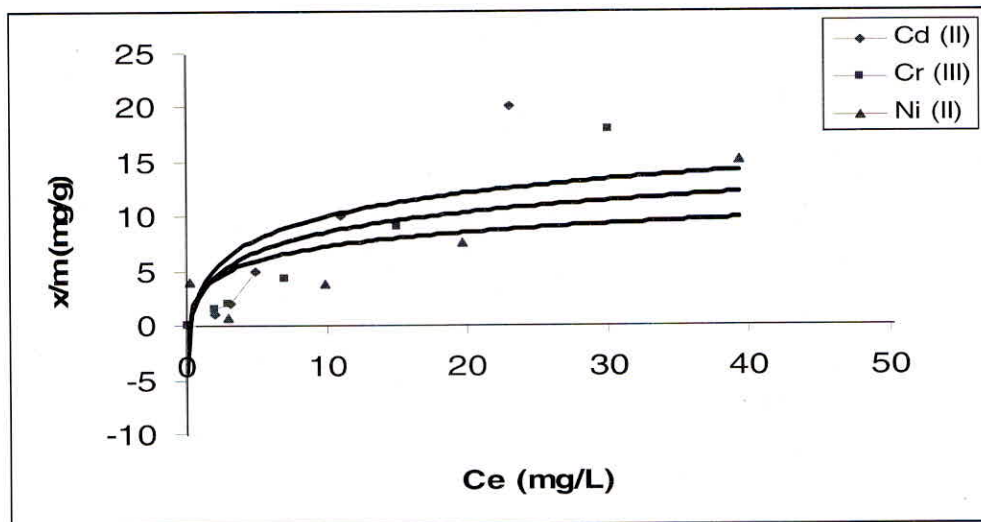


Fig. 2 : Equilibrium isotherms of ternary metal ions [Cd (II), Cr (III) and Ni (II)] on SILP. [C_0 : 25 mg/L; m: 4.0 g; pH: 6.5 for Cd (II), Cr (III) and Ni (II)].

Cr (III): 74.82% and Ni (II): 42.78%]) was found to be lowered (10-20%) as compared to the case of single metal ions reported in our earlier publications. Similar trends of effect of metal concentration, sorption time, biomass dosage, particle size and pH on biosorption efficiency were observed in ternary metal solution as compared to solution of single metal ions. The order of sorption of toxic metals on the SILP: obtained in our case is as follows: [Cd (II)>Cr (III)>Ni (II)] which is again similar to that of single metal ion solutions. The decrease in sorption capacity of same biomass in target metal solution than that of single metal ions may be ascribed to the less availability of binding sites. In case of multi metal solution, the binding site is competitively divided among the various metal ions. The combined action of competitive biosorption of [Cd (II), Cr (III) and Ni (II)] seems to be antagonistic in nature. The most logical reason for this action was claimed to be screening effect by the metals present in the solution (Sag and Kutsal, 1996).

One of the important aspects for the evaluation of sorption process as a unit operation is the equilibrium of sorption. The L type nature of the equilibrium isotherm curves obtained (Figure 2) in our experiments indicates favorable environment for ternary metal adsorption. The adsorption capacity (q_e) for the ternary system [Cd (II): 0.93 mgg⁻¹ Cr (III): 0.89 mgg⁻¹ and Ni (II): 0.68 mgg⁻¹] remained lower than that for the single metal ions [Cd (II): 1.45 mgg⁻¹ Cr (III): 1.23 mgg⁻¹ and Ni (II): 0.79 mgg⁻¹] and can be ascribed to the overlapping of adsorption sites of respective metal ions. There exist a variety of binding sites on the biomass that are partially specific for individual metal species (Horsfall *et al.*, 2003).

Kinetics experiments showed that the adsorption of present ternary metals increases with the lapse of time. The adsorption of target cationic metallic species was rapid during 10 to 30 min of contact time after which the rate slowed down as the equilibrium approached 30 min of contact time. No further increase in sorption was observed with further increase of contact time up to 40 min. Adsorption rate constant (K_{ad}) was determined from the following first order rate expression: $\log (q_e - q_t) = \log (q_e) - (K_{ad}/2.303) t$, where q_e and q_t (mgg⁻¹) are the amount of target metals adsorbed per unit mass of SILP at equilibrium and at time t respectively. K_{ad} (min⁻¹) was calculated from the slope of the linear plot of $\log (q_e - q_t)$ versus time (Figure. 3). The lower adsorption rate constant (K_{ad}) for ternary metal ions [Cd (II): 0.35 min⁻¹, Cr (III): 0.36 min⁻¹ and Ni (II): 0.23 min⁻¹] compared to single metal ions [Cd (II): 0.57 min⁻¹, Cr (III): 0.47 min⁻¹ and Ni (II): 0.32 min⁻¹] might be explained that metal ions compete for vacant sites and within the shortest possible time uptake by binding sites (Reddad *et al.*, 2002).

In order to design the proposed process of sorption more economical, attempts were made to regenerate the metal-treated biomass for its effective reuse. Desorption/Regeneration studies also help in the elucidating the mechanism of metal ion removal from metal-loaded adsorbent. In general, the desorption of metal ions from metal loaded biomass are investigated using acidic, basic and neutral solutions. However, highest desorption of metal ions from metal-loaded biomass has been observed in acid media

(Wankasi *et al.*, 2005). In acidic medium, carboxyl [In the present case], carbonyl or hydroxyl group in the biomass become protonated and thus does not attract the positively charged metal ion. Therefore, desorption behavior of ternary metals from metal loaded biomass was observed after eluting with two mineral acids (hydrochloric and nitric acid) separately. The maximum desorption [Cd (II): 94.56%, Cr (III): 91.67% and Ni (II): 92.78%] was observed at hydrochloric acid (0.05 M). However, better desorption [Cd (II): 99.24%, Cr (III): 98.45% and Ni (II): 99.68%] could be achieved with the same strength of nitric acid as eluant (Table 2). Sorption of ternary metals on regenerated SILP remained constant to the value [Cd (II): 79.34%, Cr (III): 74.82% and Ni (II): 42.78%] up to three regeneration cycles and then started decreasing [Cd (II): 71.26%, Cr (III): 69.10% and Ni (II): 39.51%] in the 4th cycle. The adsorption of ternary mixture of heavy metal solution onto the surface of unmodified *Saraca indica* leaf powder (SILP) was found to be competitive type where the adsorption capacities of the metals were lower (10-20%) with those of single metal ions.

CONCLUSIONS

SILP provide an exciting opportunity under the domain of Green Chemistry for domestic, environment friendly, low cost method for decontamination of toxic metals from aqueous system, particularly for rural and remote areas. SILP efficiently removes ternary metal ions with the selectivity order of [Cd (II)>Cr (III)>Ni (II)]. The adsorption process followed a first order kinetics. The spent biosorbent was regenerated and effectively reused, making the adsorption process more economical.

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